Platinum Anode

2005-03-05

Daniel Lawton, a friend in the US, was kind enough to give me a generous length of Platinum/Iridium alloy wire for my (pre)chlorate cell experiments. An initial primitive lash-up cell resulted in a melt down, the high resistivity of the Pt/Ir wire melting and charring the lid of the cell and the sealant used to secure it in place and protect the anode connection from the spray.

After a bit of head scratching I sealed the joint between a piece of thick Cu wire and the Pt/It wire inside a glass tube and then coiled the wire back around the glass. This design waterproofed the copper connection to protect it from corrosion and placed the hottest part of the wire deep in the solution for cooling.

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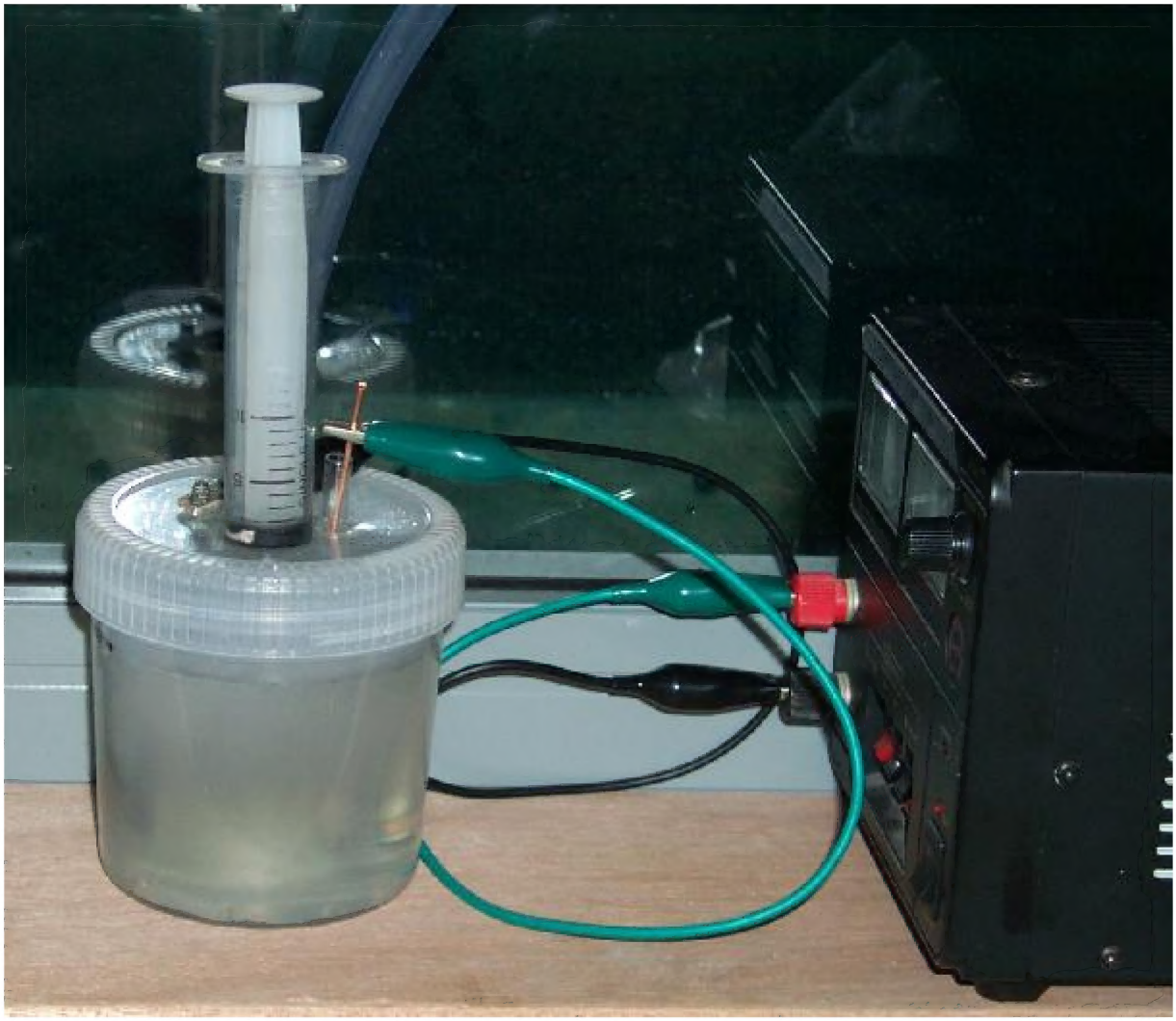
The cell was rebuilt with a new 500 ml PE jar, the graphite cathode from the proof of concept cell and a similar vent and syringe top-up facility. 400 ml of saturated KCl solution was added and a current of 4 A run through the cell.



The chlorine production was very low. Unlike the previous cell that had a very noticeable chlorine smell only moments after operation, this cell could be run without the vent pipe. No significant chlorine was produced at all. The vent was kept in place however to dump the hydrogen safely and as before act as reflux condenser to limit water loss.

Running at 4 A the cell temperature stabilized quite high, about 75 C, too hot to touch the walls for any length of time. Towards the end of the run the cell resistance had risen allowing the PSU to deliver more current to it efficiently, this caused the cell to boil, and about half its volume was lost before I noticed and readjusted the PSU and made up the lost volume.

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The cell ran from the 2005-02-20 to 2005-02-02 240 hours plus or minus a few minutes. At an average of 4 Amps that is 960 Ah.

Electrolyte Processing

The electrolyte and crystals were transferred to a 1 litre beaker and diluted to 800 ml. Heating dissolved all the crystals and the solution was allowed to boil for 20 minutes to destroy any hypochlorite keeping the volume near 800 ml - however this was probably unnecessary, the warm electrolyte straight out of the cell did not bleach unbleached filter paper and smelt only very faintly of chlorine.

The electrolyte was filtered hot through doubled papers to remove the slight graphite contamination in suspension and put back on the boil to reduce to 600 ml. The filtering leached some of the tannins from the paper staining the solution slightly. Once boiled down it was left on the window sill to cool, then it went into the fridge to crystallise out fully. (Note the "boiling chips" which are actually several cylindrical Alumina milling media - they were recovered from the raw crystals by sieving.)

A large amount of crystals came out and were filtered off. An extra 20 g or so was recovered by boiling down the filtrate to 200 ml and putting it in the fridge. The raw crystals were washed and tested free of Chlorides with Silver Nitrate solution. The remaining liquid did precipitate Silver Chloride and was returned to the "mother liquor" container along with the washings for future use despite its slightly yellow colouration. The colouration will likely be rapidly destroyed in-cell in future KCl-KClO3 runs.

A quick recrystallisation and drying gave a 200 g yield of sugary white crystals.

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Some Math

It takes 6 Moles of electrons to make 1 Mole of KClO3 from 1 Mole of KCl at 100% electrochemical efficiency. A Mole of electrons is a Faraday or an Avogadro's Number (6.0221415e23) of them. One Coloumb is one Ampere-second or 6.241506e18 electrons passing by. So a Faraday is 96485.4 Coloumbs or 26.8 Ampere-hours. Therefore it takes about 160 Ah to make 1 Mole of KClO3 from 1 Mole of KCl at perfect efficiency.

The solubility of KCl at room temperature is around 400 g/l. So the 400 ml of electrolyte contained at most 160 g of KCl. KCl's molar mass is 74.551 g/mol, so the electrolyte contained around 2.146 Moles of KCl. Total conversion of 2.146 mol of KCl to 2.146 mol of KClO3 (about 263 g) would require around 343 Ah, a bit over 3.5 days at 4 A.

As my yield was 200 g and took 960 Ah that places the efficiency at a woeful 27%! Even if we assume I failed to extract or lost 60 g of KClO3 (unlikely its solubility is around 100g/l tops and significant amounts of chloride ions were shown to be present in the liquor) that only puts the efficiency at about 36%.

Comments

Definitely better than the last run. The yield was pretty good, but the efficiency wasn't that great. The low chlorine loss is an interesting and useful effect of using a Platinum anode. I didn't weigh the anode before and after, but it was obvious that it was completely unaffected by service in the cell.

The graphite cathode has quite a significant resistance, as does the Platinum wire. My next cell will be using a Titanium cathode, so the graphite losses and contamination will be gone but the anode losses will remain a bit of a problem. Current through the cell doesn't change no matter how lossy the electrodes are you just need more voltage to achieve the same current, so I guess electrode losses are no big deal on small (non-industrial) scales. At least the I^2R losses keep the cell nice and warm.

I should do some basic calometric tests with nichrome heater to get a rough thermal resistance figure for the cell. With that I can probably estimate the I^2R losses for the electrodes and start designing effective passive thermal control rather than just guessing. The external wiring gets quite warm too, I should use a thicker gauge.

I doubt the I^2R losses are to blame for the poor efficiency, it is probably more an electrochemical inefficiency perhaps due to the large electrode spacing. Closer electrode spacing would offer higher electrochemical efficiency, but the lower impedance of the cell will require PSU changes. I wonder if stirring would increase the reaction rate too?

Also notable was the much more severe damage to the PE jar in this run. The boiling probably didn't help, the higher temperatures for extended periods cross-linking the polymer. Below the electrolyte surface the walls crazed quite badly and became frosty in appearance. Above the water line the walls became quite opaque. The jar now feels brittle and could probably be crushed in one hand. Next time I'll use PP or

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make a very nice cell, but I suspect a large Erlenmeyer flask with a three or four-hole stopper is more in my price range. I think I'll try using a thistle tube as the top-up system, although the syringe is cheap and simple it has to be removed to fill.

Update 2005-03-25

The product from this run has since been tested with Methylene Blue and found to contain significant amounts of Potassium Perchlorate despite the low solubility of Potassium Chlorate once formed. The graphite anode run product was also tested and found to contain no detectable Potassium Perchlorate.

10 comments.

Parent article: Making Chlorates and Perchlorates.

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